Direct Electrolytic Reduction of Oxides

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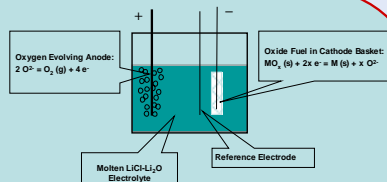
Introduction

- **Goal:** Extend pyroprocessing to include treatment of spent light water reactor fuel to reduce burden on repository
  - Recover actinides for consumption as fuel in advanced fast reactor
  - Produce durable, leach-resistant waste forms to encapsulate fission products
- Successful development of a process to reduce actinide-oxides to metals is a key step in achieving the goal
- Direct electrolytic reduction selected for conversion of spent actinide oxides to metals because of high product quality, high throughput, simple engineering, and compatibility with electrorefiner technology
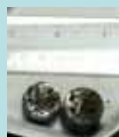

Argonne chemist tests metal oxide conversion process

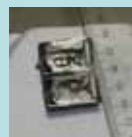## Direct Electrolytic Reduction – Process Description

Electrochemical process converts metal oxides to metals, a solid-state transformation, using electrons

Oxygen Evolving Anode: $2\ O^{2-} = O_2\ (g) + 4\ e^-$

Oxide Fuel in Cathode Basket: $MO_x\ (s) + 2x\ e^- = M\ (s) + x\ O^{2-}$

Molten LiCl-Li$_2$O Electrolyte

Reference Electrode

UO$_2$ Feed   **Partially Reduced Product**   **Fully Reduced Product**

Direct Electrolytic Reduction Demonstrated with UO$_2$ and UO$_2$-5wt% PuO$_2$ Feeds
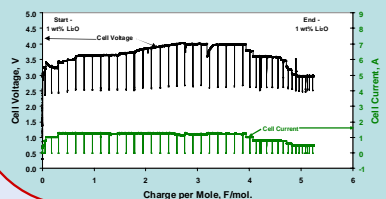

UO$_2$ Reduction with Periodic Current Interrupts – Stable Cell Performance Achieved

UO$_2$ Reduction Mechanism by Coulometric Titration

Electrochemical reduction of UO$_2$ involves multi-step electron transfer reactions

Formation of Intermediate Phases Possible

- Electrochemical evidence of multiple stable rest potentials characterizing electrolytic reduction of UO$_2$
- Formation of intermediate compounds such as Li$_2$U$_x$O$_y$ may explain the observation of stable rest potentials in UO$_2$ reduction
- For an oxide, M$_x$O$_y$, the postulated solid-state reduction mechanism is summarized by the reaction sequence:

$$M_xO_y\ (s) + z\ e^- + z\ Li^+ = Li_zM_xO_y\ (s)$$
$$Li_zM_xO_y\ (s) + (2y-z)\ e^- + (2y-z)\ Li^+ = x\ M\ (s) + 2y\ Li^+ + y\ O^{2-}$$
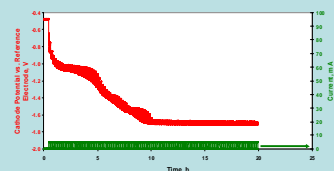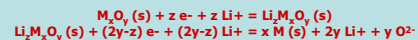
High-Capacity Reduction (HCR) Cell

HCR cells designed to provide electrochemical engineering data needed for pilot-scale cell design

Anode Assemblies

Port for Fuel Basket (Cathode)

Port for Salt Sampling and Reference Electrode

Copper Cooling Coils in Off-Gas Train

Heat Shield

Stainless Steel Reaction Vessel

HCR cells handle kg-scale feeds and large volumes of evolved oxygen

HCR Cathode Product

- Complete conversion of 1kg UO$_2$ feed to U-metal
- Entrained salt in product ~12 wt%
- Stable and reproducible cell performance
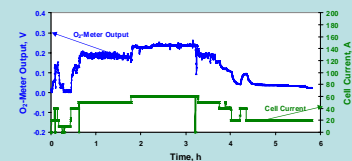
Tracking Reduction in HCR Cells

Monitoring O$_2$ in off-gas reveals reduction status and *in-situ* current efficiency

HCR Test Results

- **Instantaneous Current Efficiency**
  $$\eta = i_{O_2}/i$$
  where i_{O_2} = instantaneous O$_2$ flux (current equivalent)
  i = instantaneous cell current

  Average Current Efficiency – 65%
  - 465 Ah passed
  - 300 Ah theoretical required for 750 g UO$_2$

- **Total Oxygen Removed from Cell**
  $$\omega = \int i_{O_2}\ dt$$
  Extent of Reduction
  - 99.5% by chemical analysis of product
  - 97% by integrating instantaneous oxygen removed from cell

Summary

- Direct electrolytic reduction demonstrated using
  - UO$_2$
  - UO$_2$-5wt% PuO$_2$
- Demonstrated >99% conversion of UO$_2$, PuO$_2$, and AmO$_2$
- Reduction rates are very good
- UO$_2$ reduction mechanism involves multi-step electron transfer reactions
- HCR cells have incorporated enhanced O$_2$-handling and process monitoring features